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Comparison of the performance of several recent hydrogen combustion mechanisms

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ABSTRACT

A large set of experimental data was accumulated for hydrogen combustion: ignition measurements in shock tubes (770 data points in 53 datasets) and rapid compression machines (229/20), concentration–time profiles in flow reactors (389/17), outlet concentrations in jet-stirred reactors (152/9) and flame velocity measurements (631/73) covering wide ranges of temperature, pressure and equivalence ratio. The performance of 19 recently published hydrogen combustion mechanisms was tested against these experimental data, and the dependence of accuracy on the types of experiment and the experimental conditions was investigated. The best mechanism for the reproduction of ignition delay times and flame velocities is Kéromnès-2013, while jet-stirred reactor (JSR) experiments and flow reactor profiles are reproduced best by GRI3.0-1999 and Starik-2009, respectively. According to the reproduction of all experimental data, the Kéromnès-2013 mechanism is currently the best, but the mechanisms NUIG-NGM-2010, ÓConaire-2004, Konnov-2008 and Li-2007 have similarly good overall performances. Several clear trends were found when the performance of the best mechanisms was investigated in various categories of experimental data. Low-temperature ignition delay times measured in shock tubes (below 1000 K) and in RCMs (below 960 K) could not be well-predicted. The accuracy of the reproduction of an ignition delay time did not change significantly with pressure and equivalence ratio. Measured H_2 and O_2 concentrations in JSRs could be better reproduced than the corresponding H_2O profiles. Large differences were found between the mechanisms in their capability to predict flow reactor data. The reproduction of the measured laminar flame velocities improved with increasing pressure and total diluent concentration, and with decreasing equivalence ratio. Reproduction of the flame velocities measured using the flame cone method, the outwardly propagating spherical flame method, the counterflow twin-flame technique, and the heat flux burner method improved in this order. Flame cone method data were especially poorly reproduced. The investigation of the correlation of the simulation results revealed similarities of mechanisms that were published by the same research groups. Also, simulation results calculated by the best-performing mechanisms are more strongly correlated with each other than those of the weakly performing ones, indicating a convergence of mechanism development. An analysis of sensitivity coefficients was carried out to identify reactions and ranges of conditions that require more attention in future development of hydrogen combustion models. The influence of poorly reproduced experiments on the overall performance was also investigated.

1. Introduction

The elementary reactions of the combustion of hydrogen are a central part of the mechanisms which describe the combustion of all hydrocarbon and oxygenated hydrocarbon fuels. Moreover, hydrogen is an important fuel in itself in areas like the carbon-free economy, in fuel safety issues, and for rocket propulsion. In accordance with its high significance, several new hydrogen combustion mechanisms were published in the last decade. In these publications, agreement between measurements and simulations is usually characterized by plots, in which the experimental data and the simulation results are depicted together. However, quantitative agreement of the simulation results with the experimental data has not been investigated. A quantitative evaluation allows for

the determination of experiments that are well estimated by simulations in contrast to those that are insufficiently described. Furthermore, strengths and weaknesses of the mechanisms in certain ranges of operating conditions can be detected. Knowing the specific behavior of a mechanism helps to reduce uncertainties in the description of experiments during mechanism development and optimization.

This paper has several novelties compared to the previous publications containing comparisons of combustion mechanisms. The comparison is performed on a very comprehensive set of experiments; various measurement types (ignition delay time, flow reactor, JSR and flame velocity measurements) and experimental techniques (e.g., shock tube and RCM experiments) are included in the analysis. All important hydrogen reaction mechanisms published in the last decade are considered, as well as syngas and hydrocarbon oxidation mechanisms that were previously used to describe hydrogen reactions. The performance of all of these reaction mechanisms is compared in detail, and the conclusions drawn are supported by objective numbers.

2. Methodology

In this work the agreement of experimental and simulation results is investigated using the following objective function

$$E_i = \frac{1}{N_i} \sum_{j=1}^{N_i} \left(\frac{Y_{ij}^{sim} - Y_{ij}^{exp}}{\sigma\left(Y_{ij}^{exp}\right)} \right)^2$$

$$E = \frac{1}{N} \sum_{i=1}^{N} E_i$$

Where

$$Y_{ij} = \begin{cases} y_{ij} & \text{if } \sigma(y_{ij}^{exp}) \approx \text{constant} \\ \ln y_{ij} & \text{if } \sigma(\ln y_{ij}^{exp}) \approx \text{constant} \end{cases}$$

Here N is the number of datasets and N_i is the number of data points in the ith dataset. Values y_{ij}^{exp} and $\sigma(y_{ij}^{exp})$ are the jth data point and its standard deviation, respectively, in the ith dataset. The corresponding simulated (modeled) value is Y_{ij}^{sim} obtained from a simulation using an appropriate detailed mechanism. If a measured value is characterized by absolute errors (the scatter can be considered independent of the magnitude of y_{ij}), then $Y_{ij} = y_{ij}$. We used this option for laminar flame velocities and measured concentrations. If the experimental results are described by relative errors (the scatter is proportional to the value of y_{ij}), then we used the option $Y_{ij} = \ln y_{ij}$, which is characteristic for ignition time measurements. Error function values E_i and E are expected to be near to unity if the chemical kinetic model is accurate, and deviations of the measured and simulated results are caused by the scatter of the experimental data only. Note that due to the squaring in the definition of E, a twice as high deviation of the simulated and experimental values of one mechanism in comparison to another leads to a four times higher value of E. This objective function has been used in our previous studies on the estimation of rate parameters from experimental data [1–3].

In addition to the average error function E, another quantity was used to analyze the behavior of the mechanisms. The average absolute deviation D is defined with the absolute deviation of an individual data point D_{ij} as:

$$D_{ij} = Y_{ij}^{sim} - Y_{ij}^{exp}$$

$$D = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{N_i} \sum_{i=1}^{N_i} D_{ij}$$

using the same transformation as mentioned above. In contrast to E, the sign of the difference $Y_{ij}^{sim} - Y_{ij}^{exp}$ is maintained in the definition of D. Trends such as systematic under- or over-prediction are thereby captured in the D_{ij} values.

It is possible to characterize the similarity of simulation results using different mechanisms by calculating correlation coefficients based on the values of D_{ij}. Similar to the definitions of E and D, correlation coefficients C are calculated for each dataset and then averaged over all of the N datasets (if more than one concentration was measured in an experiment, e.g., in a flow reactor or JSR, correlation values are first determined for each species separately and then averaged). In this averaging step, datasets with $N_i \leqslant 2$ were not considered as they would perturb the average correlation values with unrealistic values (-1 or $+1$). Correlation of the individual error function values would not provide the same meaningful information about the similarity of two mechanisms, since the sign of the deviation is lost due to squaring. Hence, a positive and a negative deviation of exactly the same extent would give a correlation value of $C = 1$, which is misleading. Also, the average deviation D is not suitable for the comparison of the agreement between the experimental and simulation results using different mechanisms, since at the two summations of the D_{ij} values large positive and negative deviations might even out.

3. Mechanisms

Our aim was to test all major hydrogen combustion mechanisms that were published since 1999. Table 1 contains the list of the investigated mechanisms. Multiple mechanisms from the same research group were tested only if the older mechanism is conceptually different from the newer one. Otherwise, only the latest mechanism was considered. For instance, three mechanisms published by the Galway group were included in the mechanism comparison. Hereby, the hydrogen core of the NUIG-NGM-2010 mechanism is an extension of the previous model (ÓConaire-2004) since the bath gas helium was added. Furthermore, some of the reaction rates differ substantially between the three mechanisms, e.g., for the reaction H + O2 = O + OH. Given the importance of this reaction, these changes result in significant differences in the simulation of the hydrogen combustion chemistry. Further differences are detailed in [4]. The latest mechanism of this group, Kéromnès-2013, also features a sub-model for the reactions of the excited OH radical (OH*) largely based on the work of [5] and updated by [6]. These reactions have shown to be of high importance for a more accurate reproduction of shock tube ignition studies at high temperatures (e.g., those reported in [7]).

The hydrogen subset of reactions in the Li-2007 mechanism is identical to their hydrogen mechanism published in 2004 [8], however, the 2007 version seems to be cited more often in the recent literature, which is the reason why this name was used in the present work. In the further references to the mechanisms, an identifier (as listed in Table 1) is used, which combines the name of the first author(s) or the research group, and the year of publication.

Some of these mechanisms were originally developed for the description of hydrogen combustion [9–12], but we investigated also other mechanisms that were developed for syngas combustion [4,13–19], or the combustion of hydrocarbons or oxygenates [20–26]. For the latter mechanisms, Table 1 refers to the number of species and reactions of the hydrogen combustion part of these mechanisms; values in brackets define the size of the original mechanisms. The program MECHMOD [27] was used to remove unnecessary species and reactions describing the carbon chemistry from the mechanisms.

All mechanisms are able to describe the combustion of hydrogen–air mixtures and thus are able to handle N₂ as a bath gas.